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THE GENERAL PRINCIPLES UNDERLYING METAMORPHIC PROCESSES

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CONTENTS

PART I

INTRODUCTION

EFFECTS OF TEMPERATURE AND PRESSURE ON SYSTEMS SOLID-SOLID
- General Considerations
- Importance of Rate of Transformation
- Enantiotropic Transformations
  - Enantiotropic Transformation of Mix-Crystals
- Phenomenon of Allotropy
- Monotropic Transformations
- Geologic Thermometer
- Reactions in Systems Solid-Solid

EFFECTS OF TEMPERATURE AND (UNIFORM) PRESSURE ON SYSTEMS SOLID-FLUID
- General Considerations
- Dependence upon Character of Compression

EFFECT OF UNIFORM PRESSURE ON MELTING-POINTS

EFFECT OF UNIFORM PRESSURE ON SOLUBILITY
- Importance of Solubility Relations

LAW OF MASS ACTION AND THE REACTION CONSTANT
- Constant Solubility Product
- Salt Hydrolysis

PART II

- THE PHASE RULE
  - Qualifications in Relation to Metamorphic Systems
  - Illustrations: System $CaO-Al_2O_3-SiO_2$
    - System $CaCl_2-MgCl_2-H_2O$
  - Consideration of an Ideal Case
- GENERAL EFFECTS OF NON-UNIFORM COMPRESSION
  - Effect on Solid Phase Alone
  - Effect on Systems Solid-Liquid
    - Derivation of the Formula
  - Effect on Solubility
  - Application to Metamorphic Processes
  - Effect on Reactions with Vapor Phase
- METAMORPHISM WITH ADDITION OF MATERIAL
- CONCLUSION

PART I

INTRODUCTION

The term metamorphism in its widest sense includes all the alterations which occur in solid rock; it therefore comprises those processes which change the composition (mineral or chemical), structure, and texture of rocks after they have been formed, no matter what may have been their origin—by solidification from magma, consolidation of chemical precipitates, or mechanical deposit. But we, following Grubenmann, shall limit this somewhat and consider as typical cases of metamorphism only those in which the effects produced by the alterations determine completely the character of the rock mass.

An essential characteristic of metamorphic alterations is that the rock *as a whole* remain solid during the process. This condition does not hold whenever the original rock has at any instant been wholly melted; such a case is merely a solidification under special conditions from a magma, and the rock formed in this way is indistinguishable from an eruptive rock. When once a rock has been completely melted, we can say nothing of its particular history previous to that time; in especial we cannot know whether any of the components of the rock have existed previously as solids.

The crystalloblastic structure[1] described by F. Becke and by U. Grubenmann could not be accounted for if the new-formed rock had been formed out of a completely fluid medium, but is easily correlated with all the other properties of rocks formed by metamorphism if we regard the change to be the result of a process of melting (or of solution) which at any instant is local and partial only.

Metamorphism of rocks is effected by change of temperature, of uniform pressure, of stress, and of concentration; it occurs whenever the original components become unstable by reason of the changed external conditions, provided always that the velocity of reaction is appreciable. The above are the important factors in determining any chemical equilibrium, so that in the study of metamorphic processes it is necessary only to apply well-known physico-chemical principles to these special, and in general complicated, systems; indeed a beginning in this direction has already been made, in the well-known work of Van Hise, Becke, Grubenmann, and V. M. Goldschmidt.

The opinion has been held that physico-chemical principles are incompetent to account completely for the phenomena of metamorphism, for the reason that the system is in many cases not in a state of true equilibrium, either during the process of metamorphism or after alterations of the system have practically ceased. This lack of stable equilibrium is due to the small rate of reaction under the particular conditions, and hence is part of the large physico-chemical problem of the relation between rate of reaction and the general properties of the system or of its components.

To grasp the general effects produced by the various agents concerned in metamorphic processes is easy, even though quantitative data are still lacking; but the application of these principles to particular cases demands a clear and well-defined knowledge of their effectiveness and limitations, in order that effects may not be attributed to causes which are incompetent to account for them. The present paper is an endeavor to discuss the validity, the limitations, and the relative importance of the general principles involved; our aim has been, in bringing them definitely to the attention of geologists, to show that it is no simple matter to apply these principles, simple in themselves, to the very complicated systems encountered under geological conditions, and that very careful reasoning is required if correct conclusions are to be reached. We wish to emphasize especially the distinction which must be made between uniform pressure and non-uniform compression or stress. The importance of uniform pressure, and the magnitude of the effects producible by it, have frequently been overestimated, while on the other hand insufficient account has been taken of the comparatively much greater effects which may result from the action of non-uniform compression.

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[1] It is to be remarked that the words *Textur* and *Struktur* have a signification in German which is different from the meaning usually attached to their equivalents in English. According to contemporary German usage, which is based on the definitions given by Becke and Grubenmann, *Textur* is arrangement in space, while *Struktur* is used to express genetic relationship. Hence crystalloblastic structure has nothing to do with textural relationships such as are observed in flow cleavage; for instance, the structure of the massive eclogites is typically crystalloblastic.

We shall not go into the various kinds of metamorphism—regional-, contact-, dynamo-metamorphism, etc., for in all cases the final effect is determined by the same factors, namely, temperature, pressure, stress, chemical composition,[1] and speed of reaction. One factor may be predominant in one kind of metamorphic process, another factor in a second; but by combination of the above factors, all of the observed effects attributed to metamorphism may be accounted for.

In the following pages we present a discussion of the most important general principles involved, especially of those principles which have not always been applied correctly by those who have made use of them. We have, for the sake of clearness, divided up the subject-matter under a number of headings, to which we have, however, deemed it inadvisable to adhere strictly throughout; these are intended to be read only in the light of the general context, as it was impracticable to insert always the qualifying phrases required to render the statements strictly accurate. Moreover, this paper does not pretend to completeness, either from the chemical or from the petrologic side; it aims to treat the various topics only in so far as they are important in regard to metamorphic processes.[1]

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[1] By this is to be understood the gross chemical composition of the whole system at the period of metamorphism, and not the chemical composition of the rock-mass now.

Furthermore, the references to previous work are in no wise to be understood as a bibliography of the subject; they are given merely as illustrations, or expansions, of the ideas in the text, and have been chosen from the work with which the writers happen to be most familiar.

In pursuance of this plan, we give first a brief discussion of the general effects of temperature and pressure, followed by sections dealing with the general behavior of systems when exposed to (1) uniform pressure, (2) non-uniform compression or stress. Chemical composition is always specific and characteristic of the particular system; therefore it cannot be discussed in a general way, but must be ascertained by experiment for each system. A similar remark applies to rate of reaction.

EFFECTS OF TEMPERATURE AND PRESSURE ON SYSTEMS SOLID-SOLID[2]

General considerations.—A very large number of all crystalline substances exist in more than one crystalline form;[3] thus silica appears in at least seven distinct forms, sulphur in at least four solid forms, and so on. And it is a matter of common knowledge that further and more extended investigation always swells the list of polymorphic substances; so that it would appear as if polymorphism were the rule rather than the exception, at least with inorganic substances, especially with those of geologic interest. Let us consider what happens when we heat very slowly a substance capable of existing in more than one polymorphic form; and for the sake of simplicity, let us assume that the substance exists only in two forms, which we may designate as α and β. This assumption of only two forms really implies no limitation of generality, for even with a substance which may be obtained in more than two forms we are dealing with only two of them in the neighborhood of any single transformation temperature. Now as we slowly heat the α form, we find a slow but continuous change in its physical properties:[1] e.g., in density, refringence, and (in general) axial ratios; this gradual change goes on, until finally we observe a much more marked change of properties—which may take place either at a definite temperature or within a small range[2] of temperature—denoting that the transformation into the β form has been effected. Further heating now is accompanied anew by a gradual change of properties, a change characteristic of the β form and bearing no necessary relation to the corresponding changes shown by the α form.

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[1] For fuller information on the chemical topics the reader is referred to textbooks of theoretical chemistry: the more elementary books of Walker, *Introduction to Physical Chemistry* (Macmillan), or Senter, *Outlines of Physical Chemistry*, the larger general works of Ostwald, *Allgemeine Chemie*, or Nernst, *Theoretische Chemie*, or the more special books, such as Roozeboom's *Heterogene Gleichgewichte* or those in the series edited by Ramsay and published by Longmans; on the petrologic side, to books such as Harker, *Natural History of Igneous Rocks*, Elsden, *Principles of Chemical Geology*, and especially to Grubenmann, *Die kristallinen Schiefer*. Doelter's new *Handbuch der Mineralchemie* is a collection of observations, rather than a critical discussion of the subject, and it is not entirely free from errors of interpretation.

[2] Throughout this paper the term solid is used to designate *crystalline* material, as distinct from amorphous material (glasses); the latter are merely subcooled liquids, which differ from ordinary liquids only in that their viscosity is almost immeasurably greater.

[3] A fairly complete list of the instances known up to 1893 will be found in Arzruni, *Physikalische Chemie der Krystalle* (Braunschweig, 1893).

If now we cool again through the transformation temperature, the α form may or may not appear. Failure to reappear may be due to one of two causes: (1) that *under the particular conditions* the rate of transformation of β into α is extremely slow, or, in other words, the attainment of equilibrium requires a long time; (2) that the equilibrium between β and α is such that β is the stable form throughout the temperature range in question; consequently α can then not appear no matter how much time is allowed.

Transformations belonging to the first class—that is, where equilibrium can be attained from either side—are known as *enantiotropic;* changes which are irreversible are called *monotropic*. We shall discuss these separately; but before doing so, we wish to direct attention to a point which, though important, is often lost sight of.

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[1] A much more profound, though continuous, change is of course possible, e.g., on heating zeolites and other hydrous minerals (see F. Rinne, *Fortschritte Min.*, 1913 (3), 159–83).

[2] At least, if the rate of heating has been small.

Importance of the rate of transformation.—The point in question is that the factor which determines the actual experimental result may be the rate at which equilibrium is established under the particular conditions. We must therefore always ascertain whether the observed result is, or is not, due to a laziness—as opposed to an inability—to react; in other words, we must distinguish carefully between cases of true and *apparent*, or false, equilibrium. Lack of care in this matter may lead us to consider a transformation to be monotropic or a given form to be stable under conditions where it really is metastable, its persistence in either case being merely the result of a slow rate of transformation.

As an illustration, take the system represented by the scheme $2H_2+O_2 \leftrightarrows 2H_2O$, a system which has been so thoroughly investigated[1] that we know the conditions of equilibrium at all temperatures up to 2,600°. These conditions are such that at all temperatures below 1,000°, the pressures of oxygen and hydrogen which can exist in real equilibrium with water are infinitesimally small;[2] hence, if *real* equilibrium obtained, it would be altogether impossible to preserve in presence of water an appreciable amount of a mixture of oxygen and hydrogen. In other words, this system is, theoretically, absolutely unstable; *practically*, however, hydrogen and oxygen may be left in contact together with water for an unlimited time at ordinary temperatures, and still show no signs of reaction, which begins only at fairly high temperatures, i.e., when its velocity becomes appreciable.

This case is instructive also in showing that there is no necessary parallelism whatever between the "affinity" of two substances for one another (which is measured by the change of free energy accompanying a reaction) and the rate of reaction under any particular conditions. Thus the above reaction does not go (except at high temperatures), although the energy change accompanying it is one of the largest known; on the other hand, many reactions with comparatively feeble energy changes go quite readily. Moreover, if there were a definite connection between heat of reaction and rate of reaction, the existence of endothermic compounds would appear to be highly improbable, if not impossible.[1]

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[1] See Nernst, *Theoretische Chemie;* Bjerrum, *Z. physik. Chem.*, LXXIX (1912).

[2] Thus the extent of dissociation is of the order of 10^{-25} per cent at 25°, 10^{-5} per cent at 700°, and does not reach a magnitude which is directly measurable until about 1,200°, where it is about 0.02 per cent.

The rate of reaction varies enormously with the temperature, in general doubling for a rise of 10°. A rise of 100° therefore causes a reaction to go about one thousand times faster, while its speed is increased about a million times when the temperature is raised about 200°. In accordance with this we find that the rate of transformation of one crystal form into another tends to be greater the higher the temperature at which the transformation takes place.[2] There is very little direct evidence with regard to the effect of pressure on the rate of reaction (as distinguished from its effect on the position of equilibrium); such as there is indicates that it has little, if any, effect.[3] In any case it is a safe assertion that the effect of pressure on the rate is absolutely negligible as compared with the enormous acceleration produced by change of temperature.

The rate of a reaction is quite generally much affected by the presence of certain specific substances; thus, palladium black brings about the union of oxygen with hydrogen around 100°. Such substances affect only the rate at which equilibrium is established, but are usually understood to be without influence on the position of equilibrium; they are commonly grouped together, for convenience, as *catalysts*—a term used to conceal our present lack of knowledge of the mode of action of the majority of them. In some cases it is known that the catalytic agent acts merely as a solvent, hence producing its characteristic effect; as examples, we have the use of sodium tungstate in accelerating the reciprocal transformations of the forms of silica, and the effect of water on mixtures of calcite and aragonite—and still more, of water containing carbon dioxide, in which the solubility is greater—in converting aragonite into calcite at 100° or lower, whereas in the dry state the rate of conversion is not appreciable until temperatures around 400°. The action of many catalytic agents is known to depend upon the formation of unstable intermediate products, but for a very large number the mechanism of their action is still unknown.

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[1] There is a relation between the explosibility of such metastable gaseous mixtures and the heat change accompanying their reaction.

[2] There is of course in principle absolutely no difference between a reaction and a transformation, the latter including the processes of fusion, sublimation, and vaporization as well as the change from one crystal form to another; all are amenable to the same thermodynamical reasoning. The only differences are in the number of components, which cause corresponding differences in the equations expressing the relations quantitatively, the qualitative relations being deducible from the phase rule.

[3] Doelter (*Handbuch Mineralchemie*, I [1912], 604) estimates the influence of pressure on speed of crystallization to be great for the reason that crystallization is hastened by shaking or knocking; this inference, however, is incorrect, because he fails to distinguish between uniform and non-uniform pressure, attributing to the former effects which could only be produced by the latter.

It is essential, then, that we bear in mind, on the one hand, the distinction between the theoretical state of equilibrium and, on the other hand, that actually attained under a given set of conditions together with its dependence upon the rate of reaction under those conditions. Indeed, we may say that in a very large number of cases the reaction velocity is the decisive factor in determining the final state, though of course the *direction* in which the reaction proceeds is determined by the energy relations, under the specific conditions of the experiment, of the various substances involved.

Enantiotropic transformations.—Enantiotropic transformations are those in which equilibrium can be attained from either side, and mark the transition of one perfectly stable form into another. The rate of transformation varies enormously from one substance to another, or for a single substance even from one transformation to another. As an illustration take the substance silica:[1] quartz, when heated to 575° goes over quite sharply into another form (β-quartz), but both its transformation to tridymite at or near the inversion point (870°), and the change of the latter to cristobalite at 1,470°, proceed very slowly. There is as yet no means of prognosticating the rate of transformation; except that one may hazard the general statement that, for any single substance, those inversions which are accompanied by the slightest changes of crystal form tend to proceed most rapidly, while the rate of transformation is small wherever the change of crystal form is large.

The temperature at which an enantiotropic transformation takes place is always perfectly definite, although it may appear to lack definiteness when equilibrium is established only slowly; it is affected by the presence of impurities if the system is homogeneous, and by uniform pressure, this effect being altogether analogous to that observed with melting-points, and subject to the same thermodynamical formulation. So far as we are aware, no experimental study has been made of the influence of uniform pressure on the transition point of any system solid-solid of direct geological interest;[1] but if the appropriate data were known, this effect could be calculated with sufficient exactness from the equation

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[1] C. N. Fenner, *Jour. Wash. Acad. Sci.*, II (1912), 471.

$$\frac{\Delta T_2}{\Delta P_2} = \frac{T(V_\beta - V_\alpha)}{41 \cdot 30\, Q}$$

whereby ΔT_2, the change of transition point produced by a change of pressure, ΔP_2 (reckoned in atmospheres), is expressed in terms of Q, the heat of transformation in calories per gram, T, the temperature of transformation at 1 atm., and V_α and V_β, the respective volumes (in c.c.) of 1 gram of substance before and after the transition at T. Unfortunately, however, the requisite data, especially the values of Q, are known in very few instances, and are altogether lacking for the inversions of geologic significance. It is perfectly obvious, therefore, that one may just as well guess the final result as calculate it from the formula, using *assumed* values of the constants involved.

In passing, it may be observed that there is no general parallelism between Q and the volume change $\Delta V = (V_\beta - V_\alpha)$. Thus potassium bichromate has an inversion point at about 240°, accompanied by a large volume change but by only an inappreciable heat effect.[2] On the other hand, during the inversion of cuprous sulphide at 79° considerable heat is evolved, and yet ΔV is only about 0.0001 c.c. per gram.[3]

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[1] The effect of pressure on the equilibrium between the various solid forms of water has been investigated by Bridgman (*Proc. Am. Acad.*, XLVII [1912], 441; *Z. anorg. Chem.*, LXXVII [1912], 377); the case of sulphur, which was studied by Tammann (*Krystallisieren und Schmelzen*), is discussed in most textbooks. Some observations have also been made on the effect of pressure on liquid-crystalline transformations, which, however, resemble melting-points much more than they resemble any transitions of geologic interest.

[2] Mitscherlich, *Pogg. Ann.*, XXVIII (1833), 120.

[3] Hittorf, *ibid.*, LXXXIV (1851), 1; Tammann, *Krystallisieren und Schmelzen* (Leipzig, 1903), p. 40.

Transformation points solid-solid are presumably not affected by unequal pressure,[1] which is equivalent to a shearing stress; in this respect they are unlike melting-points. For where melting occurs, the pressure will be greater on the solid than on the liquid phase, owing to the flowing-away of the latter; at transformation points, on the other hand, where both are solid phases, they must be equally subject to the pressure, and therefore the comparatively *large* effects produced by unequal pressure on melting-points will be absent at inversion points.[2] Nevertheless it is entirely probable that persistent unequal pressure (differential stress) might increase the rate of inversion $\alpha \rightarrow \beta$, the latter being the form normally stable at high temperatures; for it is conceivable that unequal pressure in sufficient amount should lower the melting-point of the α-form to such a point that an actual progressive melting[3] of α takes place followed by a crystallization to the β-form, if that were the form stable under these particular conditions.

To illustrate, there are a number of metastable forms (for example, yellow HgI_2 at temperatures below *ca.* 120°, yellow PbO below *ca.* 550°) which can be changed into the corresponding stable forms merely by scratching or rubbing in a mortar.[4] This mode of action of unequal pressure recalls that of catalytic agents, and may be used to aid in accounting for the fact that metamorphic processes occurred easily in those regions which have been exposed to stress.

Enantiotropic transformation of mix-crystals.—We must call special attention to a circumstance which is often neglected although it is of great importance in petrogenetic systems: namely, that the temperature of an enantiotropic inversion has a single definite value only when both the forms involved in the equilibrium are simple phases and not mix-crystals (solid solutions). This same reservation holds for melting-temperatures, and is there well known. When a mix-crystal of the α-form undergoes enantiotropic change into a mix-crystal of the β-form, there is in general a *temperature-interval*, in which the α and β forms may coexist in real equilibrium. As the temperature changes within this region, there is a continuous change in the composition of the mix-crystals, which are in equilibrium with one another, precisely as in the melting of mix-crystals or the distillation of binary liquid mixtures, and for the same reason.[1] The position of this temperature interval is dependent upon the composition of the possible solid solutions, and may be displaced considerably if the corresponding inversion temperatures of the end-members of the series of mix-crystals are far apart.

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[1] The idea of "unequal pressure" and its consequences are discussed more fully in a later paragraph.

[2] Nevertheless, there might be some comparatively slight effect; for if the process of transition occurred through a melting (as is outlined in the next sentence in the text), the *difference* between the effects of such unequal pressure on the melting-points of the α and β forms would be its net effect in changing the temperature of inversion.

[3] By this it is not meant that the whole of α should at any instant be melted; see a later paragraph.

[4] It is of course possible that the slight local rise of temperature produced by grinding also plays a subsidiary role in this process.

As an illustration consider the system HgI_2-$HgBr_2$ and its inversion tetragonal→orthorhombic.[2] At 127° red tetragonal HgI_2 changes into yellow orthorhombic HgI_2; $HgBr_2$ is known only as the white orthorhombic form, so that the inversion point of the tetragonal form, if it exist at all, must be at a low temperature. From melts containing both components there separate out a continuous series of orthorhombic yellowish-white mix-crystals ($n\ HgI_2 \cdot m\ HgBr_2$); but the mix-crystals containing little $HgBr_2$ invert at low temperatures into a tetragonal modification. The temperature at which this inversion begins is lower the richer the mix-crystals are in $HgBr_2$; hence the reason that mixtures rich in $HgBr_2$ exhibit no inversion point is in all probability that the velocity of transformation at the equilibrium temperature—which then must be below 0°—is inappreciable. When a mix-crystal of the composition 9.5 mol. per cent $HgBr_2$, 90.5 mol. per cent HgI_2, is cooled slowly (care being taken that the rate of transformation is sufficiently great), it begins about 80° to change to the tetragonal form, producing tetragonal crystals approximately of the composition 2.6 mol. per cent $HgBr_2$, 97.4 mol. per cent HgI_2. Further cooling is accompanied by a progressive change of the orthorhombic into the tetragonal form with a corresponding alteration of composition of the mixtures in both modifications, until finally at about −20° the system is completely transformed into tetragonal mix-crystals of the composition 9.5 mol. per cent $HgBr_2$, 90.5 mol. per cent HgI_2. Thus at temperatures between +80° and −20° (under ordinary pressure) mix-crystals of the above composition represent an equilibrium between two modifications of different composition, either of which is completely stable in presence of the other.

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[1] See papers by N. L. Bowen, *Am. Jour. Sci.*, XXXIII (1912), 561; "The Melting Phenomena of the Plagioclase Feldspars," *ibid.*, XXXV (1913), 577.

[2] W. Reinders, *Z. physik. Chem.*, XXXII (1900), 494; P. Niggli, *Z. anorg. Chem.*, LXXV (1912), 161.

Now among the minerals of geologic importance there are many which are to be considered as solid solutions; from the foregoing, therefore, one must speak not of the inversion *temperature* of any such mineral which exists in more than one form, but only of the inversion interval. For instance, if the relation between augite and hornblende should prove to be enantiotropic (at present the nature of their relation is unknown), they could coexist in *true equilibrium* throughout a range of temperatures. It would therefore be incorrect to speak of a definite temperature, or a definite pressure, of transformation of these important minerals.

Furthermore, the modifications which coexist in equilibrium under any particular set of conditions will not have the same chemical composition. As a matter of fact, such differences have been observed in gabbros from Katéchersky by L. Duparc,[1] who gives the following analyses:

	Augite	Amphibole
SiO_2	50.91	43.34
Al_2O_3	2.64	12.60
Fe_2O_3	.....	10.44
FeO	10.07	7.92
MnO	0.41	.....
CaO	23.33	12.91
MgO	13.30	12.52
K_2O	Not determined	0.24
Na_2O	Not determined	1.90
	100.66	101.87

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[1] *Bull. soc. franc. min.*, XXXI (1908), 50. Analogous observations have been made by L. J. Wild, *Trans. New Zealand Inst.*, XLIV (1912), 333; also by J. B. Harrington, *Geology of Canada* (1879), p. 21.

The augites were considerably "uralitized" (transformed into fibrous hornblende, appearing as pseudomorphs of the augite), the process being accompanied by a marked change of composition. This interpretation of the process presupposes equilibrium conditions; but whether equilibrium conditions obtained or not, this example may serve to point out the possibility of the actual occurrence of such differences.

Closely related to the phenomena of transformation of mix-crystals is the phenomenon of allotropy, according to the latest views, which so far are the only views which aid us materially in correlating this property with other properties of the substance.

The phenomenon of allotropy.—It is well known that wherever a substance exhibits polymorphism, its various allotropic modifications may be obtained from a solution or fusion merely by varying the conditions of crystallization (e.g., rate of cooling, concentration of solvent). On this fact as foundation, a theory of allotropy has been developed by Smits,[1] the basic idea of which is that the different modifications are in reality all present in equilibrium with one another in the solution, the appearance of any one form in the solid state being determined by the conditions of this internal equilibrium, the position of which in turn is affected specifically by the solvent medium.

Let us consider, for the sake of simplicity of statement, that no foreign solvent is present, that the liquid phase is a melt of the pure substance. Such a liquid phase, which hitherto has been generally supposed to be unary (containing only a single molecular species), is considered by Smits to be pseudo-unary; that is, it contains two (or more) pseudo-components in mutual equilibrium. As a necessary consequence of the internal equilibrium in the liquid phase it follows that there is equilibrium in the solid phase between the same pseudo-components; the position of this equilibrium is, of course, not identical with that of the equilibrium in the liquid phase (just as in the case of mix-crystals). In other words, when an apparently unary liquid solidifies, even although the cooling goes on in such a way that equilibrium between the pseudo-components obtains continuously, the solid phase separating out is not a pure pseudo-component but is itself a pseudo-unary system in internal equilibrium and therefore is a mix-crystal. The solid forms actually known to us are not the pure pseudo-components themselves, but are solid phases in an equilibrium which is displaced by external circumstances toward one side or the other. The displacement of equilibrium in the solid phase produced by change of external conditions may proceed until unmixing supervenes, i.e., until an inversion point is reached.

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[1] A. Smits, *Z. physik. Chem.*, LXXVI (1911), 421, and later papers in 1912 and 1913, especially *ibid.*, LXXXII (1913), 657.

This theory has already justified itself as a working hypothesis at least; it has enabled Smits to co-ordinate certain phenomena and hence in part to predict the behavior of certain systems. This success indicates the great probability of the existence of internal equilibria, and in this respect it is in complete harmony with a number of other lines of evidence. It leads us to look upon a single crystal, not as a simple body, but as a more or less complicated configuration the behavior of which depends on the state of equilibrium within the crystal.

Moreover, it possesses a great advantage as compared with the old point of view in that it affords a clue to the problem of the apparently arbitrary appearance of metastable modifications. For if we know the diagram of such a pseudo-unary system—that is, if we know the equilibrium lines in both the liquid and the solid phase as well as the mix-crystal and liquidus curves—we can foretell which factors will promote, or hinder, the formation of a given metastable product. For instance, if the speed of attainment of equilibrium is small and the temperature change is rapid, the equilibrium will not have time to adjust itself to the changing conditions; unmixing therefore will occur at a composition (with respect to the pseudo-components) and at a temperature which differ from those corresponding to continuous real equilibrium—in other words, the resultant products in the two cases are different. The position of the various equilibrium lines and the rates at which the various equilibria are established under the particular conditions are, in short, the factors that determine which product actually appears. Hitherto the only aid in the prediction of what would appear has been that derivable from the so-called Ostwald rule,[1] a rule to which there are very many exceptions. From the above we see that the rule—in spite of its breadth—will not be generally applicable; for if it were, it would imply limitation of the type of possible configuration of the diagram of state, whereas there is no reason to believe that such limitations exist.

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[1] The rule, as stated by Ostwald, is: In all reactions the most stable state is not straightway reached, but the next less stable or that state which is the least stable of the possible states. It may be observed that this alternative mode of statement

From this point of view also we can see how the phenomena of monotropy and of allotropy are related. Whether one or the other of these phenomena occurs depends again on the position of the lines representing the internal equilibrium, especially in relation to the unmixing curves.

The foregoing brief account of the theory of allotropy proposed by Smits has been given mainly for the purpose of bringing one point to the attention of geologists and mineralogists: namely, that it aids in familiarizing us with the idea that pure phases (even crystalline) are not necessarily made up of a single molecular species, an idea which is supported by a considerable array of facts and is in conflict with no direct experimental evidence. In addition, it indicates that even metastable states, the existence of which has often been looked upon as a proof of lack of complete validity of physico-chemical principles, may also be treated theoretically.

Monotropic transformations.—Monotropic changes are irreversible; they occur when a form which is metastable under the particular conditions passes over into a form which is essentially stable under those conditions of temperature and pressure. Monotropic changes therefore occur whenever the rate of transformation becomes appreciable; moreover, since this rate is different under different conditions, the transition temperature is not a definite point but may lie within a very wide range. As an illustration consider the two principal forms assumed by calcium carbonate. All the evidence indicates that aragonite is metastable at temperatures above the ordinary; yet in the dry state it does not go over into calcite until about 400°. Yet the transition to calcite—which, being more stable, has at any definite temperature a lower vapor pressure and (in any single solvent) a smaller solubility than aragonite—takes place very slowly at 100° in presence of water, and more rapidly and at a lower temperature in presence of water containing carbon dioxide; for carbon dioxide increases the solubility of both forms, and hence the rate of transformation.[1]

The occurrence of a real monotropic change implies that one modification of the substance involved is altogether metastable throughout its range of existence.[2] But we may have inversions which appear to be monotropic, but are in reality delayed enantiotropic changes; in such cases both forms of the substance have stable fields of existence, the apparent monotropy being due entirely to the sluggishness of transformation. A good example of this is shown in the silica diagram, as determined by Fenner.[3] Quartz, when heated in presence of a suitable flux, goes over slowly into tridymite at about 870°,[4] and the change is reversible; but when the quartz is heated without a flux, it goes over into β-cristobalite, the temperature at which this transformation occurs (about 1,400° or higher) varying with the rate of heating. β-cristobalite on cooling, in absence of a flux, does not return to quartz (or go over into tridymite), but at a temperature around 200° is transformed into α-cristobalite, which therefore at ordinary pressure must be altogether metastable. Thus transformations which are sluggish may appear to be monotropic until by the choice of an appropriate solvent medium their rate is so increased that their true character can be ascertained.

The temperature at which a monotropic change takes place can be influenced only by those factors which affect the rate of transformation; it will therefore be affected by the presence of impurities when the latter can act as fluxes and in this way increase the rate, but it will be unaffected by uniform pressure, because uniform pressure apparently has little or no influence on the rate of reaction, even where the reaction is attended by a large volume change. In accordance with this we have observed that a pressure even of 15,000 atmospheres (equivalent to a depth of perhaps 30 miles) is incompetent at room temperature to convert marcasite (sp. gr. 4.9) into pyrite (sp. gr. 5.0) nor did this change take place to an appreciable extent at 425° under 2,000 atmospheres pressure, although under ordinary pressure it does take place about 450°.[1]

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[1] It is to be observed that this argument of an increased solubility being attended by an increased rate of reaction must be used with caution; it will in general hold only when the original solubility was comparatively small.

[2] At least, at ordinary pressure. At higher pressures such a modification may have a stable field of existence; though up to the present there is no direct experimental evidence bearing on this point.

[3] *Jour. Wash. Acad. Sci.*, II (1912), 471. The system silica has also been investigated by Endell and Rieke, *Z. anorg. chem.*, LXXIX (1912), 239, and by Endell and Smits, *ibid.*, LXXX (1913), 176.

[4] This is the lowest temperature at which this transformation will take place. It occurs at all temperatures up to 1470°, at which point tridymite ceases to be the stable phase and is replaced by β-cristobalite.

Geologic thermometer.—The use of transformation and other points has been suggested as fixed points on a geologic temperature scale,[2] that is, as points of reference by means of which we may be enabled to fix the range of temperature within which certain processes have occurred or certain rocks or minerals have been formed. Such points should be chosen and used with caution. The only points free from objection are those transformations solid-solid which take place at a definite point with appreciable velocity and are not much influenced by pressure; in other words, we must choose rapid transitions which are accompanied by a small change of volume (or in the rarer case, by a large heat effect; or by both together). This is a serious limitation upon the number of satisfactory points, a limitation which must, however, be retained so long as our ignorance of the magnitude and character of the compressive stresses to which rocks have been subject remains complete, as in effect it now is. Melting-points could be used as points on the geologic thermometer only by postulating the purity of the substance and on the further improbable assumption that the compression has always been uniform; for, as we hope to show in a later paragraph, the effect of unequal pressure (shearing stress) upon the melting-point is so great that no conclusion of any value can be drawn except from such transition points solid-solid as remain unaffected by compression of any kind.

The use of transitions involving a gas or vapor phase is altogether indefensible. Take for instance the dissociation of calcium carbonate, according to the equation $CaCO_3 = CaO + CO_2$; to each temperature there corresponds a definite pressure of CO_2, a pressure which varies enormously with the temperature. Unequal pressure moreover affects such dissociations to a still greater extent than it influences melting-points. Transitions involving a vapor phase therefore can be employed as reference points when, and only when, we can accurately define the character and magnitude of the compression—a condition unlikely to be fulfilled in any instance of geologic importance at any time in the immediate future.

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[1] G. Spezia (*Atti. Accad. Sci. Torino*, XLVI [1911], 1) has made a number of similar observations all of which are in complete harmony with the above statements.

[2] See Wright and Larsen, *Am. Jour. Sci.*, XXVII (1909), 421; *Z. anorg. Chem.*, LXVIII (1910), 338; J. Koenigsberger, *Neues Jahrbuch Min.*, Beilage Band XXXII (1911), 101, in which he makes a number of statements which require some reservation,

Occurrence of reactions in systems solid-solid.—This subject has been treated at some length in a recent communication from this laboratory;[1] so only the general conclusions will be presented here. Reaction may proceed at the surfaces of contact of adjacent grains of the constituents; but it by no means follows that reaction occurs in all systems where we might on other grounds judge that the stable state of the system would be that which obtains after reaction has taken place. The extent of the reaction will be increased by renewal of the surfaces of contact, and this may be effected by any agency which produces a kneading or grinding of the mass. Hence the reaction will be furthered by application of non-uniform (unequal) pressure (or in other terms, shearing stress), which moreover may also act in another way, the net result of which, however, is again to bring together new surfaces of contact. This will happen, namely, if the unequal pressure is of such character as to cause any of the original constituents or of the products of reaction to melt at the temperature of experiment; for then it will obviously further the reaction. Furthermore, non-uniform pressure can promote reaction by bringing adjacent grains into good contact; the reaction can then progress by diffusion across the area of contact. The effect of uniform pressure on reaction between solids is limited to this rôle, and therefore its effect is in general slight.

Interdiffusion of solids is appreciable in some systems: for instance, gold traveled into lead some 7 mm. in four years at room temperature, and about as far in as many weeks at 160°.[2] All the evidence indicates, however, that interdiffusion goes on only in those systems in which solid solutions can form, as indeed one might expect a priori. The diffusion is enormously accelerated by rise of temperature, and may be influenced by pressure, though it would be premature to regard this as established yet, far less to generalize from it. In any case the rate of diffusion under geologic conditions, wherever diffusion is possible at all, is probably sufficient to reduce in the course of geologic time the degree of heterogeneity of systems which originally were not too coarse grained. Nevertheless old rocks frequently show well-defined layers of isomorphous crystals which, so far as we know, can form homogeneous mix-crystals; this is true especially for plagioclases, hornblendes, augites, and garnets, and indicates that in these cases the rate of diffusion is vanishingly small.

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[1] J. Johnston and L. H. Adams. *Am. Jour. Sci.* (4), XXXV (1913), 205; *Z. anorg. Chem.*, LXXX (1913), 281.

[2] Roberts-Austen, *Phil. Trans. Roy. Soc. London*, A., CLXXXVII (1896), 383. For full information on this subject see "Report on Diffusion in Solids" by C. H. Desch, *British Assoc. Report* (Dundee, 1912); see also the recently published *Geologische Diffusionen* by R. E. Liesegang (Dresden: Steinkopf, 1913).

EFFECTS OF TEMPERATURE AND PRESSURE ON SYSTEMS SOLID-FLUID

General considerations.—In discussions of the change of volume (to take a specific instance) which accompanies the process of melting, one often encounters the argument that this change is given by the difference between the densities of the crystals and of the glass, as measured at ordinary temperature. This argument may be altogether misleading, because it involves the tacit assumption that the expansion coefficients of both crystals and glass are identical—an assumption which certainly can fit the facts only in a few exceptional cases.[1] Of course until the necessary quantities have been actually determined, one can only use the densities observed under ordinary conditions; but if one does so, the limitations of any results calculated in this way must be recognized, and the conclu-

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[1] The truth of this statement is perhaps more obvious from the following mathematical formulation. If V_l and V_s are the specific volumes of glass and crystals, respectively, at ordinary temperature, the change of volume

$$\Delta V = V_l - V_s\,.$$

The change of volume at the temperature t is

$$\begin{aligned}\Delta V_t &= (V_l + \Delta V_l) - (V_s + \Delta V_s)\\ &= \Delta V + (\Delta V_l - \Delta V_s)\end{aligned}$$

where ΔV_l and ΔV_s are the expansion produced by the increased temperature in glass and crystals, respectively. The term $(\Delta V_l - \Delta V_s)$ may be positive or negative, and might even be of such magnitude as to cause the sign of ΔV_t to be opposite from that of ΔV, if the latter were itself small.

sions regarded as tentative and preliminary only. Precisely similar remarks apply to the effect on this volume change of pressure alone or of pressure and temperature combined.

The computation of heats of reaction for conditions differing from those under which the experimental values were determined is subject to altogether analogous limitations, the specific heat, or change of heat capacity, being the exact analogue of expansion coefficient. In this case indeed we may have—although to be sure the experimental data are not very concordant—an instance of reversal of the heat effect of a reaction with rise of temperature. The heat of transformation aragonite → calcite at 20° is small, probably positive and less than 1 cal. Now according to the most thorough series of measurements for aragonite and calcite,[1] their mean specific heats within the range 0°–300° (the limit of the measurements) are respectively 0.2246 and 0.2204; hence the difference is 0.004 per degree or about 1.8 cal. for 450°. Therefore the heat of transformation at 470° will be 1.8 cal. *less* than it is at 20°, and thus a minus quantity; this is in agreement with the observations of Lashchenko,[2] who concluded that this transformation at 470° is accompanied by the absorption of considerable heat.

Variation of effects of compression with its character.—There is a marked difference in the effect of compression according as it is uniform or otherwise. Changes in the physical properties of substances are induced by uniform pressure, but disappear when the pressure is removed. Non-uniform compression produces permanent deformation of bodies exposed to it, and therefore causes permanent alterations in many of the physical properties of the substance. The effects of the latter differ so much from, and so far outweigh those of uniform pressure, both in character and in magnitude, that it is advisable to treat them separately.

Uniform pressure is, by definition, the same in all directions; in practice, however, this is not altogether easy of attainment at really high pressures, because then the liquids generally used to transmit pressure become exceedingly viscous.[1] A non-uniform compression may always be resolved into a shearing stress and a (smaller) uniform pressure, the former being the preponderating factor in producing the results observed. Now a consistent account of all the experimental work can be given if we make the plausible assumption that the shearing stress acts on the solid phase, but not on the liquid phase; in accord with this, in non-uniform compression the liquid (fluid) phase would be subject to less pressure than the solid phase, whence the name "unequal pressure" chosen to designate this type of compression.[2]

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[1] Lindner, *Sitzber. physik. medizin. Ges. Erlangen*, XXXIV (1902), 217.

[2] Lashchenko, *Jour. Russ. Phys. Chem. Soc., XLIII* (1911), 793. It may be noted, however, that Boeke, who used a differential method, concluded that the heat change at 470° is less than 0.5 cal. (*Z. anorg. Chem.*, *L* [1906], 246).

EFFECT OF UNIFORM PRESSURE ON MELTING-POINTS

Thermodynamical considerations lead directly to the differential equation

$$\frac{dT}{dp}=\frac{TdV}{\Delta H} \tag{I}$$

which expresses the change of melting-point (dT) with change of pressure (dp) in terms of T, the absolute temperature of melting, dV, the volume change and ΔH, the heat change which accompanies melting of the substance at T. Before this equation can be applied it must be integrated, since we are dealing with finite changes.

In order to integrate this equation rigorously it is necessary to know how dV and ΔH vary with pressure and temperature. The exact magnitude of these variations is not known in general; but, fortunately, their effect is slight and may for most practical purposes be neglected. We may consequently use the following form of the equation to calculate the change of melting-point (ΔT_2) produced by a change of pressure (ΔP_2, expressed in atmospheres[3]):

$$\frac{\Delta T_2}{\Delta P_2}=\frac{T(V_l-V_s)}{41\cdot30\,Q} \tag{II}$$

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[1] For instance, at 20,000 atm. and ordinary temperatures, even gasoline becomes quite viscous (approximately, perhaps, of the consistency of vaseline).

[2] A fuller discussion of this topic, together with many references to previous work, will be found in a paper by Johnston and Adams, *Am. Jour. Sci.* (4), XXXV (1913), 205; *Z. anorg. Chem.*, LXXX (1913), 281; cf. also *postea.*

[3] That is, true atmospheres (1,033 g. per sq. cm.).

wherein Q is the heat (absorbed) of melting in calories per gram, and V_l and V_s the respective volumes of 1 gram of substance at the melting-point in the liquid and the solid state. An example of the agreement between calculation from this formula and actual observation of the effect of pressure on the melting-points of tin, bismuth, cadmium, and lead is afforded by the following table, taken from a former paper from this laboratory;[1] the divergences are such as are to be expected in view of the present uncertainty in the values of Q, the latent heat of melting:

TABLE I

EFFECT OF UNIFORM PRESSURE ON THE MELTING-POINTS OF CERTAIN METALS

Metal	Latent Heat cal. per gram Q	Vol. Change on Melting V_l-V_s	ΔT per 1,000 atm. calc. from Equation II	ΔT per 1,000 atm. observed
Sn.........	14.25	0.003894	+3.45	+3.28
Cd.........	13.7	0.00564	+6.10	+6.29
Pb.........	5.37	0.003076	+8.59	+8.03
Bi.........	12.6	−0.00342	−3.67	−3.55

Equation II enables us therefore to calculate the effect of uniform pressure on melting-point if certain physical constants of the material are known; unfortunately, however, these constants are known for very few substances, among which are practically none of direct geologic interest.

Direct determinations of the effect of pressure on melting-point have been made only as follows: potassium,[2] sodium,[3] mercury,[4] water,[5] and a large number of organic substances[6] (e.g., benzol, phenol, naphthalene, etc.) including several substances capable of existence as a liquid-crystalline phase.[7] All of these investigations show that the change of melting-point for the first 1,000 atm. is less than 40°;[1] further, that for each succeeding 1,000 atm. the effect is progressively less, a fact which indicates that no maximum melting-point is realizable (if indeed it is possible).

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[1] Johnston and Adams, *Am. Jour. Sci.*, XXXI (1911), 516; *Z. anorg. Chem.*, LXXII (1911), 29.

[2] Tammann, *Krystallisieren und Schmelzen.*

[3] *Ibid.*

[4] P. W. Bridgman, *Proc. Am. Acad.*, XLVII (1912), 349; *Z. anorg. Chem.*, LXXVII (1912), 377.

[5] *Proc. Am. Acad.*, XLVII (1912), 441.

[6] Tammann, *loc. cit.;* Hulett, *Z. physik. Chem.*, XXVIII (1899), 629 (pressures only up to 300 atm.).

[7] Hulett, *loc. cit.;* Körber, *Z. physik. Chem.*, LXXXII (1913), 45.

There are only two substances for which a lowering of melting-point by uniform pressure is established, namely, water and bismuth; and with water only at pressures up to about 2,100 atm. (where the m.p. is $-22°$), above which the melting-point rises steadily with pressure, reaching $+76°$ at 20,000 atmospheres. There may be a few other substances belonging to this category but their number is certainly small. In general, therefore, uniform pressure raises the melting-point; so that we may say that uniform pressure increases the rigidity of material—an increase which becomes very noticeable with substances (e.g., the oils commonly used to transmit pressure) whose freezing-point is not far removed from the ordinary temperature.

EFFECT OF UNIFORM PRESSURE ON SOLUBILITY

The influence of temperature upon the solubility of solids varies greatly from one substance to another; the more common effect is an increase of solubility with temperature, but there is a large number of substances (e.g., $Ca(OH)_2$, $CaSO_42H_2O$, to name two common ones) whose solubility decreases with rise of temperature. The direction and magnitude of this change of solubility is determined by the sign and magnitude of the heat of solution; an absorption of heat corresponds to an increase of solubility with temperature, an evolution of heat to a decrease. In applying this criterion, one must take care to choose the heat effect[2] appropriate to the dissolution of the particular solid phase which is in equilibrium with the solution under the particular conditions; for instance, to use the heat of solution of $Ca(OH)_2$, not of CaO, and at temperatures above 32.4° to use the (positive) heat of solution of Na_2SO_4 (anhydrous), at lower temperatures the (negative) heat of solution of $Na_2SO_410H_2O$ which is then the stable solid phase in solution.

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[1] With one exception, camphor, where 300 atm. pressure raised the melting-point by 38.7° (Hulett, *loc. cit.*).

[2] The heat effect to be used is always that observed when 1 mol. of the solid is dissolved in a large volume of a solution nearly saturated with respect to the solid in question.

The effect of uniform pressure on the solubility of solids can be calculated from an equation analogous to equation I whenever the heat effect and volume change appropriate to the particular conditions are known. Hitherto trustworthy direct determinations have been made for only four substances,[1] of which but one is even of indirect geological significance; the mean values obtained are given in the subjoined table.

TABLE II

CHANGE OF SOLUBILITY PRODUCED BY UNIFORM PRESSURE (COHEN AND COLLABORATORS)

PRESSURE IN ATMOSPHERES	$CdSO_48/3H_2O$ AT 25°		$ZnSO_4 \cdot 7H_2O$ AT 25°		MANNITE AT 24.05°		NaCl AT 24.05°	
	Conc. of Satd. Solu. g. $CdSO_4$ per 100 g. H_2O	Percentage Change	Conc. of Satd. Solu. g. $ZnSO_4$ per 100 g. H_2O	Percentage Change	Conc. of Satd. Solu. g. Mannite per 100 g. H_2O	Percentage Change	Conc. of Satd. Solu. g. NaCl per 100 g. H_2O	Percentage Change
1....	76.80	.....	57.95	.....	20.66	.....	35.90	.....
500....	78.01	+1.57	57.87	−0.14	21.14	+2.32	36.55	+1.81
1,000....	78.84	+2.68	57.65	−0.52	21.40	+3.57	37.02	+3.12
1,500....	.....	.....	.....	.....	21.64	+4.72	37.36	+4.07

From this we see that it would be likely to require a very considerable change of (uniform) pressure to change the solubility by 50 per cent, a change which may easily be produced by a comparatively small change of temperature. Hence the influence of pressure on the solubility of solids is altogether negligible in comparison with the influence of temperatures.

Uniform pressure may cause marked increase in the apparent solubility in certain cases; namely, wherever we are really dealing with an equilibrium, the state of which is displaced by pressure. An example of this is afforded by calcium carbonate in presence of water and carbon dioxide; increased pressure increases the concentration of CO_2 in the water (and hence really changes the character of the solvent) and thus produces a greater apparent solubility of the $CaCO_3$. Moreover, the solubility of solids in fluids at temperatures above the critical point of the solution will be dependent on the pressure, since the effect of the latter is then to change the concentration of the solvent, just as pressure affects the solubility of gases, by changing the concentration of the solute itself, and hence the concentration of the solute in the solution.[1]

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[1] E. Cohen and L. R. Sinnige, *Z. physik. Chem.*, LXVII (1909), 432; LXIX (1909), 102; E. Cohen, K. Inouye, and C. Euwen, *ibid.*, LXXV (1911), 257. These authors give a critical résumé of earlier work along this line.

One point remains to be noticed, namely, that in making use of solubility data we must remember that solubility, and the heat effect and volume change accompanying dissolution of a substance, are affected by the presence of other substances[2] in the solvent. Now from a complex solution from which any one of a number of substances can conceivably separate out first, the product which actually separates out is that which under the particular actual conditions is least soluble, or has reached its limit of saturation.[3]

Solubility relations are therefore of the highest importance; but they must always be determined under the proper conditions, and cannot be inferred from the relative solubilities of the various substances in pure water.

Importance of solubility relations in determining the course of a reaction in solution.—The importance of this fact—that solubility (or perhaps we should rather say, lack of solubility) is the predominating factor in determining the order of separation of the products of reaction of any system—is not so universally appreciated as it ought to be. The appearance of any one product is very often ascribed to the existence of a greater affinity between its component parts than exists between the components of the other compounds which might conceivably be formed by the reaction. In a certain sense this is true, but in the sense in which the term affinity is ordinarily employed it is fallacious and misleading. For example, consider the following reactions:

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[1] This question is discussed later.

[2] The following are two extreme examples, which illustrate the two main modes of action of added substances. $Ag(CN)_2$ is very sparingly soluble in water, but quite soluble in water containing KCN, owing to the formation in this case of the complex $KAg(CN)_2$. The solubility of AgCl, on the other hand, is much smaller in water containing KCl (or $AgNO_3$), owing to the effect of the common ion Cl' (or Ag^+).

[3] This is the basic principle underlying van't Hoff's great series of investigations of the oceanic salt deposits.

$$AgNO_3+BaCl_2 = 2\mathit{AgCl}+Ba(NO_3)_2$$
$$Ba(NO_3)_2+Ag_2SO_4=\mathit{BaSO_4}+2AgNO_3$$

From the first of these, we should, according to the above reasoning, conclude that silver was a stronger base than barium; while from the second, we reach the directly opposite conclusion.

As another example, take the statement (which appears in the majority of textbooks on organic chemistry) that tetramethylammonium hydroxide ($N(CH_3)_4OH$) cannot be displaced from aqueous solutions of its salts (e.g., the chloride) by potassium hydroxide because the former is the stronger base. But it has been shown that if we choose a medium (methyl alcohol) in which one of the products (potassium chloride) of the reaction is insoluble, the reaction

$$N(CH_3)_4Cl+KOH=N(CH_3)_4OH+\mathit{KCl}$$

takes place and yields practically the theoretical amount of the tetramethylammonium hydroxide.[1] These two examples, which are typical of a very large number of similar cases, demonstrate that the relative strength of the competing acids and bases is a negligible factor in determining the product which separates out following a reaction in aqueous (or other) solution; the important factor is the relative solubility limits of the original substances and of the possible products of reaction.[2] This behavior is in thorough accordance with the law of mass action and with the currently accepted theory of solution; so that if we knew the solubility relations of all possible products (including complex salts, e.g., the double cyanides and oxalates, if such are possible) we could predict quantitatively the course of the reaction.

Another good example, which at the same time illustrates another point, is this. If we add hydrochloric acid to a solution of sodium silicate, sodium chloride will be formed and silicic acid (in the form of gelatinous silica) liberated; but yet at a very high temperature, as in the process of glazing earthenware, silicic anhydride in presence of water vapor is capable of decomposing sodium chloride with expulsion of hydrochloric acid. This behavior is not at first sight dependent on solubility relations; but it is perfectly analogous if we consider that volatility may be looked upon as solubility in a vacuum as solvent. We can therefore extend the statement of the preceding paragraph and say that the factor which determines the result of heating together a number of substances at high temperatures is lack of solubility or of volatility, the substance which tends to appear being that which under the particular equilibrium conditions is least soluble or least volatile.

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[1] Walker and Johnston, *Jour. Chem. Soc.*, LXXXVII (1905), 955.

[2] This statement is subject to slight limitations, which, however, are of minor importance, and hence need not be discussed here. Their effect is such that a lack of concordance of 1 or 2 per cent may be found between theory and practice.

THE LAW OF MASS ACTION AND THE REACTION CONSTANT *K*

Consider the reversible chemical action

$$A+B \leftrightarrows C+D$$

where the letters represent single molecules of the substances as in ordinary chemical formulae. Then according to the law of mass action the state of equilibrium of the above system is determined by the equation[1]

$$\frac{[A]\,[B]}{[C]\,[D]}=K$$

where the symbols [A], [B], etc., represent the "active masses" *at equilibrium* of the respective substances; *K* is a constant, the value of which depends solely on the external conditions (e.g., temperature) but is independent of the total amount of material present. When the reaction takes place in a wholly gaseous system, the active mass of each substance is proportional to its molecular concentration or partial pressure. When the system is an aqueous

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[1] When the reaction is $nA+mB \leftrightarrows pC+qD$ (that is, where more than one molecule of any (or all) of the substances enters into the reaction) the expression for the reaction constant is

$$\frac{[A]^n[B]^m}{[C]^p[D]^q}=K$$

In this case attention must be paid to the unit of concentration employed except when $m+n=p+q$, as the numerical value is then dependent on the unit of concentration employed.

solution, the active mass of each reacting molecular species (which are, according to the current views, ions and undissociated molecules) is given by the concentration of that particular species in the unit of volume (expressed always in molecular, or equivalent, concentrations). It should be observed that K is found to be constant only in dilute solutions (and correspondingly, in gaseous systems only at low pressures); but there is no doubt that its lack of constancy at greater concentrations (or pressures) is due altogether to our lack of accurate knowledge of the real concentrations (partial pressures) of the reacting molecular species. The reaction constant K is independent of the amounts of the various substances originally present, so long as the temperature and pressure remain constant; its dependence on temperature (at constant pressure) is given by the equation[1]

$$\frac{d\ln K}{dT}=\frac{Q}{RT^2} \tag{III}$$

Hence if we know K at any one temperature, and the heat change Q accompanying the reaction,[2] we can calculate K at any temperature; conversely from the values of K at various temperatures, we can compute mean values of Q.

Similarly, the variation of K with (uniform) pressure, at constant temperature, is given by the equation

$$\frac{d\ln K}{dp}=-\frac{\Delta V}{RT} \tag{IV}$$

where ΔV is the increase of volume accompanying the reaction when 1 mol. is transformed. This equation holds strictly in homogeneous systems; where solid substances are present, it is essential that they be subject to the same uniform pressure as the rest of the system. The equation is the quantitative formulation of the statement that increase of pressure tends to displace the equilibrium in the direction in which the reaction is accompanied by decrease of volume.

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[1] $\ln K$ is $\log_e K = 2.303 \log_{10} K$.

[2] For exact work we must know further how Q varies with temperature; the assumption of a constant value of Q, however, leads to results sufficiently exact for most purposes. Further, our knowledge of Q at any one temperature usually leaves much to be desired, not to speak of its variation with temperature.

In a completely fluid system the influence of pressure on the position of equilibrium will not in general be large, because the volume change ΔV is usually small. In gaseous systems the direction of the effect can readily be predicted, since the volume of a gas (at constant temperature and pressure) is a direct measure of the number of molecules of it present. Therefore pressure is without effect if the total number of molecules remains unchanged by the reaction; otherwise, it displaces the position of equilibrium toward the side with the smaller total number of molecules.

In heterogeneous systems liquid-gas and solid-gas the pressure changes the concentration in the gas phase, and in this way may have very considerable effect on the position of equilibrium.

The action of *unequal* pressure, however, on a heterogeneous equilibrium is of an entirely different order of magnitude. If a system solid-liquid or solid-gas is compressed in such a way that the fluid phase can escape continuously, the reaction will be driven in one definite direction. For example, if the system

$$RCO_3+SiO_2 \rightarrow RSiO_3+CO_2$$

is compressed in such a way that the CO_2 escapes, $RSiO_3$ will always be formed. Then, too, unequal pressure influences greatly the solubilities of solids, and thus may entirely change the relative concentrations of the solid substances in the fluid phase.

The foregoing paragraphs provide a basis for the observation that metamorphosed rock is usually denser than that from which it was formed, for the so-called *Volumgesetz* of the Germans. To this rule there are many exceptions; the extent to which it holds is about what we might expect; for while pressure tends to produce denser material, it may not actually do so if the rate of reaction is very small under the particular conditions. Moreover, we cannot safely conclude from measurements of specific volume made at ordinary temperature (as all of them hitherto have been) that the change of volume under the actual conditions of transformation was the same in magnitude or even in sign; for, as we have already pointed out, a difference (such as may easily occur) between the coefficients of expansion of the substances concerned may cause a reversal of sign of the volume change, especially when the latter is small.

As an application of the law of mass action to a very simple case, consider the dissociation of calcium carbonate according to the equation

$$CaCO_3 \leftrightarrows CaO + CO_2 .$$

We will presume that the reaction takes place in the gaseous phase: the equilibrium constant is then given by the equation

$$\frac{(CaO)\,(CO_2)}{(CaCO_3)} = C \,,$$

the quantities in parentheses denoting the partial pressure at equilibrium of the substance written within the parentheses.[1] Now CaO and $CaCO_3$ are always present in the solid phase, from which it follows that at any one temperature (CaO) and $(CaCO_3)$ are constant; whence we have $(CO_2) = K$. In other words the pressure of CO_2 in equilibrium with a mixture of CaO and $CaCO_3$ is independent of the amounts of the solids present, and has a definite value for every temperature;[2] its variation with temperature being given by equation III.

E. Baur[3] has investigated a system of considerable geologic interest, namely, the reaction

$$SiO_2 + 4HF \leftrightarrows SiF_4 + 2H_2O$$

which takes place when aqueous hydrofluoric acid is distilled in presence of excess of silica. Under these conditions SiO_2 is solid, the other three substances gaseous; therefore at definite temperature and pressure we should find that the expression

$$\frac{(SiF_4)\,(H_2O)^2}{(HF)^4} = K \,.$$

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[1] It may be objected that it is absurd to talk about the vapor pressure of a substance such as CaO; we have, however, every reason to believe that such pressures, though infinitesimal, are real and perfectly definite. Application of the mass law to the vaporization of CaO, that is, to the reaction CaO (solid) → CaO (vapor), gives the relation $\frac{(CaO)}{CaO\ (solid)} = K'$; but since excess of solid is present, CaO (solid) is constant and therefore at constant temperature $(CaO) = K''$.

[2] These values may be found in Johnston, *Jour. Am. Chem. Soc.*, XXXII (1910), 938.

[3] *Z. physik. Chem.*, XLVIII (1904), 483.

The actual determination of the various concentrations is very difficult, so that moderate concordance between the values of K is all that can be expected. At 104°, K is of the order of 2×10^9, at 270° it is about 5×10^7. This decrease of K with rise of temperature shows that the equilibrium is displaced toward the left by rise of temperature, so that the reaction, as written above, is at these temperatures slightly exothermic. The influence of pressure is easily predicted; for, since we have 3 volumes on the right side, as compared with 4 volumes on the left (the volume of the solid silica is, in comparison, negligible), pressure will displace the equilibrium toward the right-hand side of the equation above. From the above it follows that, when such vapors escape from the magma, lowering of their temperature alone will result in a dissolution, instead of a precipitation, of SiO_2; decrease of pressure, on the other hand, results in the production of quartz—an effect which will presumably predominate over that produced by decrease of temperature, since the volume change is large but the heat change accompanying the reaction comparatively small.

Constant solubility product.—Again we can readily deduce from the mass-action law the experimental fact of the constancy of the so-called solubility product. Thus for the substance AgCl we find that

$$(Ag^+)\,(Cl^-)=K$$

where (Ag^+) and (Cl^-) represent the real concentrations of silver ions and chlorine ions in the solution; K is a constant, depending only upon the temperature. This relation holds true for any solution in which silver ions and chlorine ions may be present together in contact with solid AgCl—no matter what other ions may also be present—provided always that (Ag^+) and (Cl^-) are understood to be the *real* concentrations of the respective ions, when equilibrium has been attained.

As a specific example of the application of this principle to the determination of equilibrium conditions, we shall consider the reversible reaction

$$BaSO_4+Na_2CO_3\leftrightarrows BaCO_3+Na_2SO_4\ .$$

There are present in the system the following molecular species: un-ionized $BaSO_4$ and $BaCO_3$, Ba^{++}, SO_4'', CO_3'' (and Na^+, which, however, may be left out of account, since it plays no direct part in the reaction).

We have then the equilibrium equations between these quantities

$$[Ba^{++}][SO_4''] = K_1 \text{ and } [Ba^{++}][CO_3''] = K_2$$

where K_1 and K_2 are the solubility products of $BaSO_4$ and $BaCO_3$, respectively; and therefore, since $[Ba^{++}]$ is common to both,

$$[SO_4'']/[CO_3''] = K_1/K_2 = K .$$

In words, the ratio of the concentrations of sulphate ion and carbonate ion is constant. Therefore, if, after equilibrium has been attained, we add SO_4'' (as Na_2SO_4), $BaCO_3$ is transformed into $BaSO_4$, until this ratio reattains its constant value; conversely the addition of CO_3'' causes the formation of $BaCO_3$ at the expense of the $BaSO_4$. In each case the amount transformed is perfectly definite; and the state of equilibrium can always be calculated if K_1, K_2, and the concentration of either SO_4'' or CO_3'' are known. If the conditions were such that the system should become saturated with respect to sodium sulphate or carbonate (or both), the equation determining the equilibrium would be somewhat more complicated; but the general result would be the same, namely, that the position of equilibrium is determined by the relative solubilities (in the particular medium) of such of the possible products of reaction (which include the original substances) as separate out as solid phases.

On this basis we can readily see why it may be that carbonic acid may displace silicic acid from a solution of a silicate at low temperatures, while at high temperatures the silicic acid may displace the carbonic acid and regenerate the silicate; and that it is unnecessary to bring in the conception of affinity or strength of acids to account for the phenomena observed. Nor is it necessary to attribute the reversal in aqueous solution of reactions such as the above to the influence of pressure, as is frequently done. It is true that pressure is required in order to retain the volatile components, the concentration of which in the vapor phase is thus determined by the pressure; but it is limited to this more or less subsidiary rôle. The predominating factor in determining the state of equilibrium in solution is temperature, which acts primarily through its effect on the solubility relations of the substances involved in the reaction; secondarily and much less generally, through its effect on the hydrolytic dissociation of salts.

Salt hydrolysis.—It is a matter of common knowledge that the aqueous solutions of many salts are not neutral; thus for instance sodium carbonate, sulphide, and silicate are alkaline; the chlorides; nitrates, and sulphates of most polyvalent bases are acid. This behavior is attributed to a process termed salt hydrolysis, which may be represented by the reaction

$$BA+H_2O \leftrightarrows BOH+HA$$

and occurs (to an appreciable extent) only when the acid, or the base (or both),[1] is weak.[2]

It is impossible to enter here into the theory of hydrolysis, or to derive from the law of mass action the relations which determine its extent. Suffice it to say that under constant external conditions the extent of hydrolysis is perfectly definite, and depends upon the magnitude of the dissociation constant of the weak acid[3] or the weak base;[4] or rather on the relation between this dissociation constant and that of water; so that the process of hydrolysis may be regarded as a competition for the strong base (or acid) between the weak acid (or base) and water (which may exercise either basic or acidic functions). Thus in decinormal solution at ordinary temperatures: sodium chloride is practically not hydrolyzed, sodium acetate is hydrolyzed to an extent which is just appreciable (0.01 per cent), while sodium sulphide or silicate is hydrolyzed to somewhere about 90 per cent. With rise of temperature the dissociation constant of water increases faster than that of the acids and bases; consequently the extent of hydrolysis increases markedly with rise in temperature.

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[1] This case is of less practical importance, hence its consideration is omitted here.

[2] The strength of an acid (or base), in the sense in which it is used here, is measured by its extent of ionization. Thus, in decinormal solution at 25°, hydrochloric acid is ionized to about 85 per cent; acetic acid to about 1 per cent; hydrogen sulphide to about 0.1 per cent; corresponding to this the respective dissociation constants of these acids are 1 (approximately), 1.8×10^{-5} and 9×10^{-8}. The dissociation constant of water at 25° is 1.2×10^{-14}.

[3] In salts which yield an alkaline solution.

[4] In salts which yield an acid solution.

Of the hydrolysis of the silicates little is definitely known, except that the ordinary solutions of alkali silicates (water glass) are nearly completely hydrolyzed into free alkali and colloidal silica. But from this it is not quite safe to conclude that the salts corresponding to all of the silicic acids (or aluminosilicic acids,[1] if such salts exist) are also completely hydrolyzed under all conditions. For it is quite conceivable that hydrolysis of a silicate may take place without producing colloidal silica; this might occur either because the silicic acid resulting from hydrolysis of the particular silicate is not colloidal or because of the intervention of factors—temperature, or the presence of other substances in the solution—which enhance the *real* solubility of silica and thus decrease its tendency to appear in colloidal form. The extent of hydrolysis under such conditions would be that corresponding to the dissociation constant of the silicic acid, which may not be so small as is commonly supposed. For in the hydrolysis of silicates, as it has been observed, the silica becomes colloidal and is removed from true solution as fast as it forms, and hence its active mass in the solution remains exceedingly small; consequently the hydrolytic dissociation continues until practically all of the original silicate is decomposed. This therefore affords us no *certain* information as to the strength of the silicic acid, for the same phenomenon would be observed even if the silicic acid were of such strength (e.g., comparable to acetic acid) that the extent of hydrolysis is of the order of 0.1 per cent; furthermore, it is no absolute criterion of what would happen if no colloidal material were formed.

The rôle of hydrolysis is important in the kaolinization of the feldspars, and in many reactions occurring in solution in liquid water; but in all probability it is altogether subsidiary—if not entirely negligible—under magmatic conditions, in which case it is preferable to regard the silicate mixture as solvent and the water (or other gases) as solute.

Most silicates react alkaline in contact with water; but according to F. Cornu,[2] an acid reaction is given by a number of minerals, such as hibschite, kaolin, pyrophyllite, nontronite, all closely related to the kaolin formula $R_4Al_2Si_2O_9$. Now the reaction between complex silicates and water is not necessarily simple; for instance, the reaction may be due to hydrolysis of the first products of decomposition of the silicate. Moreover, atmospheric carbon dioxide might play a part in the reaction. In this connection it is well to observe that it is incorrect and useless to speak of the *solubility* of a mineral in water, unless the mineral dissolves as a whole; just as it is useless to speak of the solubility of a metal in an acid. We may speak of solubility only when the relations between the various components are the same in the solution as in the solid, or when it is possible to recrystallize the original silicate from the solution. Otherwise we are dealing, not with a process of solution, but with a decomposition.

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[1] To illustrate by means of an analogous case: the salts of hydrocyanic acid (HCN) are largely hydrolyzed, whereas there is very little hydrolysis with salts of hydroferrocyanic acid ($H_4Fe(CN)_6=4HCN, Fe(CN)_2$).

[2] Tschermak's *Mitt.*, XXIV (1905), 417.